

# CONCURRENT CHANGES IN AGGREGATION AND SWELLING OF COAL PARTICLES IN SOLVENTS

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## INTRODUCTION

The behavior of solvent-(induced) swelling of coal without complete dissolution in any solvents has been used as evidence for the three-dimensionally cross-linked macromolecular network model of coal structure. Sanada and Honda<sup>1</sup> applied the statistical theory of rubber elasticity to coal swelling. Since then coal swelling has been used to characterize the macromolecular nature of coal by many workers<sup>2-10</sup>. Four major methods have been used: the volumetric method using glass tubes<sup>1-13</sup>, the gravimetric method<sup>13,4</sup>, the method requiring a piston type of apparatus<sup>10,14,15</sup>, and direct observation using a microscope<sup>6,16-18</sup>. The easiest and most commonly used one is probably the volumetric method.

The conventional volumetric technique with glass tubes was selected to investigate the physical structure of coal in this author's recent papers<sup>19-22</sup>. Some steps in the method were modified. Coal samples and solvents were weighed, and each initial height before swelling was calculated from the mass and bulk density of the samples. This was necessary to obtain reproducible results, particularly at low coal (slurry) concentration. In the previous paper<sup>20</sup>, coal/solvent mass ratios ( $C/S$ ) were used as an index of concentration. From this study, it was found that coal swelling is strongly dependent on  $C/S$ <sup>20</sup>. The high dependence of  $C/S$  on coal swelling is very important, because changes in swelling with  $C/S$  is not thermodynamically allowed for the three-dimensionally cross-linked network model.

The results showed that swelling ratios,  $Q$ , did not change in the common range of  $C/S = 10-20$  % which is generally used for the conventional volumetric swelling method, but significantly increased at  $< C/S = 5$  %<sup>20</sup>. At the low  $C/S$ , the dependence of coal concentration on  $Q$  is given by

$$Q = [Q]/(C/S)^n \quad (1)$$

where

$$[Q] = \lim_{\log(C/S) \rightarrow 0} Q \quad (2)$$

and  $n$  is a constant.  $[Q]$  is defined as the intrinsic swelling ratio, which is independent of  $C/S$ . The  $[Q]$  values were consistently more than two times larger than those conventionally observed. Therefore, conventionally observed swelling ratios are apparent values. It is thought that intra- and intermolecular (secondary) interactions are solvated more at a lower  $C/S$  value and coal swells more. The process of attaining associative equilibria is presumably very difficult when using the volumetric method. The dependence of  $C/S$  on coal swelling means that swelling changes depending on uniformity of coal and solvent. Coal and solvent are usually mixed only at the initial time with a thin rod. It is not practical to continuously mix coal and solvent for a long time, because it may take more than 24 h to reach its equilibrium value<sup>21,22</sup>. These strongly suggest that coal swelling should be measured at a very low coal concentration with continuous mixing for a given period to avoid the effect of these unknown factors. Furthermore, measurements of volumetric swelling at low  $C/S$  values are difficult. Therefore, an apparatus specifically designed for these factors is necessary.

The objective of this paper was to observe coal swelling in solvents at low coal concentration with continuous mixing. It can be thought that coal swelling is given by the difference of particle sizes between poor and good solvents. The measurement of particle sizes in solvents by a laser scattering method is applied to the system. The swelling ratio measurement by a particle size distribution was probably first suggested by Turpin *et al.*<sup>17</sup>, but the details were not reported. The observation of coal swelling under the conditions is very important to better understanding of coal structure and also the behavior of coal particles in coal/oil systems in various processes.

## EXPERIMENTAL

Blind Canyon (DECS-16) and Illinois No. 6 (DECS-2) coals (-20 mesh) were obtained from the DOE Coal Bank at Pennsylvania State University. These pyridine extracted coals (PI) were prepared by Soxhlet extraction for 3 days. Pyridine extracts (PS) were also used. PI and PS were dried under vacuum at 95°C overnight. All samples were ground with a agate set to arbitrary particle sizes (-100 mesh). The same lots of samples were used for particle size measurements. Standard polyvinylpyrrolidone with average molecular mass of 10,000 and cross-linked polyvinylpyrrolidone were obtained from Aldrich Chemical Co. These polymers as received were used for particle size measurements.

For a new method of swelling, Model LAB-TEC 1000 particle size analyzer (LASENTEC, Bellevue, WA) was used. This analyzer is a scanning laser type of apparatus<sup>23</sup>. When the focal spot intercepts a particle, some light is scattered back to the probe and converted into an electronic pulse, which is converted to size by the relationship:

$$d = v/t \quad (3)$$

The duration of the pulse represents the time ( $t$ ) the focal spot illuminated the particle. Since the velocity

(v) of the focal spot is known, the distance ( $d$ ) for the focal spot scanned across the particle can be determined. This distance represents the length of a chord of the particle. Pulses representing the chord lengths are classified by counting circuits, then transferred to a computer for processing and presentation on a display or a printer. The LAB-TEC 1000 classifies particles into 29 channels, ranging from 0.2 to 250  $\mu\text{m}$ . The distribution is presented in two ways in this study. Scanned count is the uncorrected random chord frequency distribution. Volume diameters are the distribution of volume, derived from the scanned count data, when particles are assumed to be spherical. The mean volume diameter and the mean diameter with scanned counts are shown as  $D_v$  and  $D_c$ , respectively. LASANTEC<sup>®</sup> measuring beakers (100 ml) were used for a sample container. Samples were agitated with a magnetic stirrer during measurement.

## RESULTS AND DISCUSSION

### *Attempt of swelling ratios by particle size distribution*

The reproducibility of measurements using this particle size analyzer was confirmed with a standard powder sample provided by the manufacturer before every measurement. The critical factor to obtain reliable results was to adjust a focal point of laser to the inner wall of the measuring beaker. Once the focal point is carefully tuned, measurements of the particle size distributions were reproducible.

The particle size distribution of the PI sample from Blind Canyon (DECS-16) coal ground to arbitrary was measured in methanol and pyridine. The coal concentration was 0.25 g/100 ml (coal/solvent). Since the evaluation method using glass tubes can be used only down to the value of  $C/S = 2-3\%$ , this coal concentration was relatively low for the swelling measurement. In addition to low coal concentration, coal particles were observed with continuous mixing. Laser was continuously scanned for several hours, and the distributions averaged every 20 scans were monitored several times. This was repeated for one week after preparation of samples. Any significant change in the distributions was not observed for these measurements.

Figure 1 shows the particle size distributions of this sample with volume diameters in (a) methanol and (b) pyridine. The distribution in methanol did not significantly change with time, while that in pyridine changed from time to time. The change in the distribution in pyridine was not dependent on time but apparently reversible from time to time. Two typical distributions in pyridine are shown here. The  $D_v$  value in methanol was 120  $\mu\text{m}$ , while pyridine values were (b-1) 130  $\mu\text{m}$  and (b-2) 60  $\mu\text{m}$ . Methanol is a very poor solvent for coal, while pyridine is one of the best. The particle size distributions in pyridine were, however, approximately the same or smaller than that in methanol. This is surprising, because swelling ratios of high-volatile bituminous coals can be estimated to be more than 3 at this concentration range by the conventional volumetric method<sup>20</sup>. The above measurements were also evaluated using PI from Illinois No. 6 (DECS-2) coal. General results obtained from the DECS-16 coal were again similar for this sample.

### *Particle size distribution of standard polymers*

To confirm the above proposed mechanism, the particle size distribution of standard polymers was evaluated under the same conditions. Fine powders of polyvinylpyrrolidone (average molecular mass; 10,000) and cross-linked polyvinylpyrrolidone as received were used. Polyvinylpyrrolidone readily dissolves in methanol and water, but does not dissolve in *n*-hexane and toluene. Toluene is a slightly better solvent than *n*-hexane. The distribution in toluene changed from time to time, and two representative distributions are shown. Mean volume diameters determined were 14  $\mu\text{m}$  in *n*-hexane and 18 and 31  $\mu\text{m}$  in toluene, respectively. The difference between these distributions is small, but the change in particle sizes with larger diameters is seen in toluene. The change was apparently reversible. The particle size distribution of cross-linked polyvinylpyrrolidone was evaluated next in methanol and *n*-hexane. Figure 2 compares these distributions with scanned counts at a concentration of 0.50 g/100 ml (polymer/solvent). As a significant portion of particle volume diameters exceeded 250  $\mu\text{m}$ , the distributions with scanned counts are presented. The specific swelling ratio ( $Q^*$ )<sup>20</sup> of this sample in methanol and *n*-hexane were 4.0 and 3.0, respectively. This suggests that methanol is a better solvent than *n*-hexane and swells the polymer. Therefore, the particle size of this polymer in a good solvent (methanol) was expected to be larger due to swelling. The results, however, shows that particle sizes in methanol ( $D_c=34\ \mu\text{m}$ ) are actually smaller than those measured in *n*-hexane ( $D_c=53\ \mu\text{m}$ ). One interpretation is that this cross-linked polymer is initially swollen in methanol but concurrently disaggregates. The overall particle size distribution may reflect these adverse effects.

It was notable that particle sizes of pyridine extracted DECS-2 and -16 coals observed in pyridine and methanol were nearly equal, considering the volumetric swelling in pyridine was much larger than in methanol. Apparent reversible changes in the particle size distribution of coal were observed in pyridine. The results obtained from standard polymers are consistent with these results.

### *Change in numbers of coal particles in solvents*

From the above results, the following behavior of coal particles in solvents is suggested: Coal particles are highly aggregated even at the relatively low  $C/S$  values. Coal particles are swollen, but interparticle disaggregation also occurs in good solvents. This may lead to apparent small coal swelling in good solvents observed by particle size distributions. If this interpretation is correct, numbers of coal particles should be different between poor and good solvents. Numbers of coal particles can be measured as numbers of light scattered back to the probe by this apparatus.

The numbers of particles of the P1 from DECS-2 coal were evaluated in methanol, toluene, chloroform and pyridine at concentrations of 0.1 - 0.5 g/100 ml. Figure 3 shows the accumulated channel % for  $\leq 1.3 \mu\text{m}$ . Obviously, coal particles with small diameters increased in the order of better solvents for coal; methanol, toluene, chloroform and pyridine at all concentrations tested.

#### *Effect of coal concentration on the particle size distribution*

Volumetric swelling increases at low coal concentration<sup>10</sup>. The evaluation method using glass tubes was used down to the value of  $C/S = 2-3\%$ . The particle size distribution was investigated to evaluate the effect of coal concentration at further low values. Volume diameter distributions for the DECS-16 coal were measured in coal concentration from 1 g to 0.1 g per 100 ml pyridine. Since the dependence of coal concentration on volumetric swelling was remarkable below  $C/S = 2-3\%$ , a notable increase in the particle size would be expected at the concentrations of 1 to 0.1 g/100 ml. No significant increase in the particle size with a decrease in coal concentration was found, but a decrease in the particle size is noted at lower coal concentrations. These results again demonstrate the significant variance in coal swelling observed by two different procedures; the volumetric swelling and the particle size distribution methods. The results can be interpreted on the bases of the proposed mechanism. Coal particles may swell at low coal concentration to large extent, but interparticle disaggregation due to a decrease in coal concentration seems to control the overall particle size distribution.

#### CONCLUSIONS

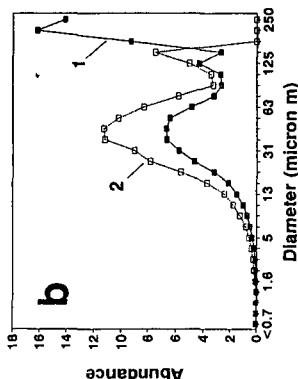
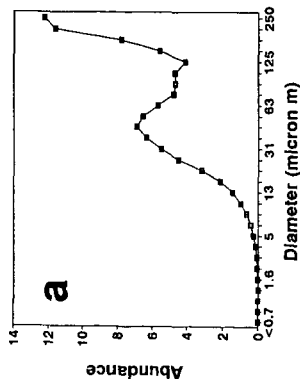
A new method of coal swelling has been developed under the condition of low coal concentrations with continuous mixing of coal and solvent. The change in particle size distributions by a laser scattering procedure was used for the evaluation of coal swelling. Particle size distributions in good and poor solvents were nearly equal, but reversibly changed in good solvents from time to time. It was concluded that aggregated coal particles disaggregate in good solvents, and that an increase in the particle size distribution due to swelling in good solvents are compensated by a decrease in the particle size due to disaggregation. Therefore, the behavior of coal particles in solvents is controlled by aggregation in addition to coal swelling. This implies that an increase in the particle size due to coal swelling in actual processes is not so large as expected by the results obtained from the conventional coal swelling methods.

#### ACKNOWLEDGEMENT

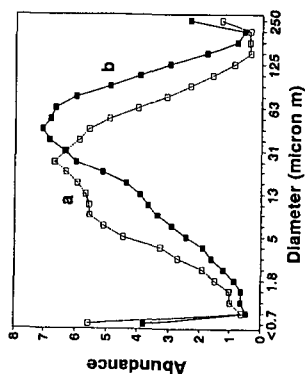
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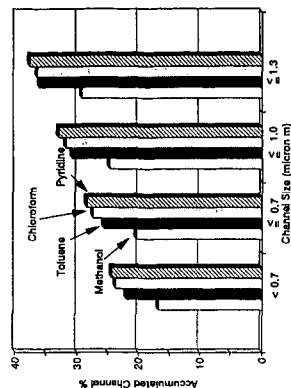
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**Figure 1** Particle size distribution with volume diameters of the pyridine extracted DECS-16 coal at coal/solvent = 0.25 g/100 ml, (a) in methanol ( $D_v$ , 120  $\mu\text{m}$ ), (b-1) in pyridine ( $D_v$ , 130  $\mu\text{m}$ ) and (b-2) in pyridine at another scanning ( $D_v$ , 60  $\mu\text{m}$ ) (average of 20 cycles)



**Figure 2** Comparison of particle size distributions with scanned counts of cross-linked polyvinylpyrrolidone at sample/solvent = 0.50 g/100 ml, (a) in methanol ( $D_c$ , 34  $\mu\text{m}$ ) and (b)  $n$ -hexane ( $D_c$ , 53  $\mu\text{m}$ ) (average of 20 cycles)



**Figure 3** Accumulated channel % for channel sizes of  $\leq 1.3 \mu\text{m}$  for the PI sample from DECS-2 coal